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WORKPLAN FOR TASK 2.8

Particle Size Distribution Analysis for the California Regional PM10/PM2.5 Air Quality Study

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Aerosol Dynamics Inc., December 11, 2002

Overview

This task is comprised of 6 subtasks, as described below. Our tentative schedule is given below. It assumes data availability by the beginning of 2003. The background, and a description of each subtask is outlined below.

TASK 2.8 Workplan Schedule.

	Subtask 2.8.1 Internal Consistency	Subtask 2.8.2 Modal Char.	Subtask 2.8.3 Spatial/ Temporal Variability	Subtask 2.8.4 Synthesis, Publication	Subtask 2.8.5 Vertical Profiles	Subtask 2.8.6 Reporting
Start	Jan-03	Apr-03	Jun-03	Aug-03	Nov-03	Sept-03
Completion date	Mar-03	Jun-03	Aug-03	Oct-03	Nov-03	Dec-03

1. Introduction

Distributions of ambient particles with respect to their size were first reported by Junge. He modeled the frequency distribution of the number of particles as a function of the logarithm of their diameter in accordance with an inverse power law [$dN/d\log D_p = kD_p^{-n}$], where the exponent *n* is 3. The smaller the particle, the more abundant, without limit. While it was clearly expected that at some size, below that which could be measured, the number distribution would show a maximum, this form was used to approximate airborne particles for several decades.

The first advance on the Junge size distribution came with Whitby et al. (1972, 1980), based on measurements made in Los Angeles, California as part of ACHEX, the aerosol characterization experiment. Whitby advanced the view of the bimodal distribution. This was found by plotting the volume moment of the distribution, that is the volume (or mass) of particles as a function of diameter, rather than the number concentration that had

been plotted by Junge. These two modes were identified as coarse and fine, with a separation at about 2 μm. The coarse mode is found to be composed of dust, sea salt and mechanically generated particles. It is found to be nearly independent of the fine mode, which is formed by photochemically and combustively generated particles. The fine mode was further divided into accumulation and nuclei modes, with a division at approximately 0.1 μm. The nuclei mode referred to directly emitted particles below 0.1 μm. These would quickly coagulate and "accumulate" in the range between 0.1 and 1 μm. The accumulation mode also contains secondary aerosols, formed either by condensation of condensable species from the gas phase or by droplet reactions.

The next advance in the understanding of atmospheric size distributions also came as a result of studies in the Los Angeles Basin. The first glimpse came from the analysis of impactor size distribution data. In 1982, McMurry and Wilson advanced the idea of inferring particle formation mechanisms from the size distribution, and used this idea in the analysis of power plant plumes and smog chamber studies. Later that year Hering and Friedlander (1982) reported the classification of sulfate size distributions in Los Angeles into two types, one formed by droplet reactions and one formed by homogeneous gas phase reactions with subsequent condensation. Then, in 1988, based on measurements during the ARB-sponsored nitric acid study, John and coworkers (Wall et al., 1988) identified the modes reported by Hering and Friedlander in all their ion distributions, including nitrate, ammonium ion and sodium, as well as for sulfates. They first named these the "droplet" and "condensation" modes, with analogy to the relationship between formation mechanisms and size as identified by McMurry and Hering.

The concept of "droplet" and "condensation" modes was not applied to total, physical size distributions until the Southern California Air Quality Study (SCAQS). In analysis of the SCAQS data, Hering et al. showed that Whitby's accumulation mode is not a single mode, but is comprised of two modes. By a combined analysis of impactor, optical particle counter and electrical mobility size distributions, Hering et al. showed that the two components of the accumulation mode could be identified as the "droplet" and "condensation" modes, exactly as found in the ionic species size distribution measurements. Key to this analysis was the consistency in the physical size distribution measured by a combination of optical particle counters and electrical mobility analyzers to that inferred from the sum chemical species size distributions measured by impactors.

Most recently, advances have been made in understanding the structure of the size distribution below 0.1 μm. Urban measurements in Atlanta have found new particle formation in the nanometer size range (McMurry, 2001). Advances have also been made in measuring the physical characteristics of ambient particles, and how these influence physical size distribution measurements. Kreisberg et al. (2001) report how relative humidity influences physical size distributions and the effective particle refractive index. Hand et al. (2001) show the consistency among several measurement techniques: a laser optical particle counter, a differential mobility optical particle size spectrometer, and a micro-orifice impactor.

In CRPAQS, size distributions were measured for the purpose of providing high-time resolution measurements of particle concentrations, and to provide insights into size-

dependent variability in those concentrations. The concentrations of particles in the nuclei mode, below 0.1 μm, are commonly attributed to fresh emissions. The data from CRPAQS will allow this hypothesis to be tested. These same nuclei or ultrafine particles have been implicated in effects on human health. Thus, it is important that their concentrations be quantified, even though they are not a significant contributor to the PM2.5 mass. Size distributions are also important to visibility. With simultaneous measurements of particle scattering and size distributions, it can be determined whether fluctuations in visibility are attributable to changes in particle concentration or in their size distribution. Size distributions may elucidate the dynamics of particle formation and transport.

For these reasons, size distribution measurements were considered an important part of the CRPAQS program plan. However, no single instrument is capable of measuring particle concentrations over the entire size range of atmospheric interest. Thus, several types of instruments were used. The measurement principle, and the type of sizing, varies with each of these instruments. The data set generated is complex and large. Knowledge of the instruments is needed to integrate these diverse measurements into a coherent data set, and to extract integral parameters that may be readily utilized.

2. Scope of Work

Task 2.8 asks the following two questions:

> "What are the particle size distributions and particle number counts?"
> "How do they vary in space and time?"

These questions will be addressed through 7 subtasks, as described below:

Subtask 2.8.1. Internal Consistency Evaluation

Before directly addressing the questions of Task 2.8, the size distribution data will be examined at Level 2, that is, the data will be validated through comparison of like measurements. Physical size distributions were measured with three different instruments, each covering different size ranges, and each based on different measurement principles or significant variations on the same principle. These data sets will be compared in their regions of overlap. Throughout the study period, the consistency of the integrated size distributions will be evaluated by comparison of inferred particle scattering coefficient to that directly measured by nephelometry. Physical size distributions will be compared to the sum of species size distributions measured by impactor when available.

Subtask 2.8.2. Modal Parameter Characterization

The three size distribution instruments produce approximately 80 channels of data every five minutes. More meaningful are the modal parameters of the size distribution, including the particle number, volume, and geometric mean size characteristic of each size range, or mode. Additionally, the distributions will be characterized by their moments, defined as a integral over the distribution weighted by a power or function of the particle diameter. These parameters give concise information about different portions

and aspects of the size distribution. They will be abstracted from every size distribution. This will provide a characterization of the size distribution data by a set of parameters that can be more readily interpreted. This task will directly answer the first question of Task 2.8, namely what the size distributions are.

Subtask 2.8.3. Spatial and Temporal Variability

The spatial and temporal variability of the size distributions will be directly evaluated for the modal parameters obtained in Subtask 2.8.2 above. Of specific interest will be the variability in the moments of the distribution. Total number concentration, reflects the concentration of the nuclei mode, and may be expected to be highly dependent upon the proximity of local combustion sources. The surface area is most sensitive to the accumulation mode of the aerosol, and is expected to be dependent upon overall synoptic conditions. Particle mass is directly related to the third moment of the distribution, the particle volume. This subtask directly addresses the second question listed under Task 2.8, namely characterization of the temporal variability. Assessment of spatial variability will be limited to a comparison of the two sites with size distribution data.

Subtask 2.8.4. Synthesis and Publication

The spatial and temporal variability of individual modes of the size distribution will be compared with that for specific chemical components measured with high time resolution. Of interest is the comparison of nuclei mode particles with black carbon mass, and of accumulation mode volume with nitrate concentration. A manuscript for journal publication will be prepared on results of these first three tasks.

Subtask 2.8.5. Vertical Profiles for Coarse Particles at Angiola

At Angiola, coarse particle size distributions were measured at three heights, on the ground and at two heights on the tower. These coarse particle distributions will be compared in terms of their modal parameters, namely number concentration, particle volume, geometric mean diameter and geometric standard deviation. Results will be communicated to those engaged in detailed analysis of the coarse particles and their vertical distributions through Task 5.3.

Subtask 2.8.6. Reporting

As requested in the call for proposals, we will deliver a draft work plan, monthly reports and a final report. A journal manuscript will be prepared under subtask 2.8.4. The final report will be submitted in Acrobat and Word format as requested, together with ten hard copies.

3. Technical Approach

3.1. Subtask 2.8.1: Internal Consistency

Several instruments were used to measure the particle size distributions or to measure an integral moment of the distribution. The first step in the analysis of the size distribution data is the evaluation of the internal consistency in these data.

The instruments used for size distribution measurement are listed in Table 1. The TSI scanning mobility particle sizer (SMPS) measured size distributions over the size range from 10 nm to 400 nm (0.4 μm). This instrument sizes particles based on their electrical mobility, which for spherical particles is directly related to their physical size and electrical charge. Particles from 0.5 μm to 10 μm were sized using a Climet optical particle counter, which sizes particles based on the light scattering per particle. The intermediate size range, from 0.1 to 2 μm, was spanned by a laser optical counter, the PMS LasAir. These instruments were operated on the ground at Angiola, and at the Fresno First St. monitoring site. Size distributions were measured throughout the study period, and reported in 80 size channels every five minutes.

For selected periods during intensive operation days of the winter intensive, micro-orifice impactor (MOUDI) samples were collected for 6-hr integrated measurement of the size distribution of organic carbon, elemental carbon and inorganic ions and gravimetric mass. The MOUDI has 8 stages that collect particles in 8 size fractions between 0.1 and 10 μm. They were operated with an after-filter to measure the concentration of particles below the lowest, 0.1 μm, cutoff. Although the size resolution of the MOUDI is not as detailed as the SMPS and optical counters, the MOUDI has the advantage of a consistent type of

Table 1. Particle Sizing Instruments for CRPAQS

Instrument	Parameter	Size Range	Measurement Principle	Schedule, Time Resolution	Fresno	Angiola	Angiola Tower, 50m	Angiola Tower, 100m
TSI Scanning Mobility Particle Spectrometer (SMPS)	number distribution	0.01-0.4 μm	electrical mobility	continuous, 5 min resolution	X	X		
PMS LasAir	number distribution	0.1-2 μm	single particle light scattering	continuous, 5 min resolution	X	X		
Climet Spectro	number distribution	0.5-20 μm	single particle light scattering	continuous, 5 min resolution	X	X	X	X
MOUDI	chemical species mass distribution	<0.1, 0.1-18 in 8 stages	impactor	selected 6-hr periods during IOPs	X	X		
Radiance Research Nephelometer	particle light scattering coefficient at or below 65% RH		ensemble light scattering	continuous, 5 min resolution	X	X	X	X

sizing over the entire size range. When available these data will provide a valuable comparison to the physical size distribution measurements. Table 1 also lists the nephelometer, which measured the particle light scattering coefficient at relative humidity of 65% or less. This measurement can be related to an integral over the size distribution for an assumed value of the particle refractive index.

With this data set, three types of Level 2 data validation checks are possible:

- Comparison of the overlap region between SMPS (mobility) and LasAir optical counter, and between the LasAir and Climet optical counters;
- Comparison of reconstructed light scattering with nephelometry;
- Comparison of the MOUDI and physical size distribution measurements.

Some of these comparisons have been made for the winter intensive at the Fresno site by Watson et al. (2001). They found that the SMPS saw 28% fewer particles than the LasAir in the region of overlap during the winter intensive, and that this discrepancy was lower at larger number concentrations. They also saw that the light scattering calculated from the size distribution measurements compared well with that measured for summer months, but was lower than measured for the winter. It is noted that the wintertime measurements were confounded by heating of the particle sample stream because the particle sizing instruments were housed inside the monitoring station. Comparisons have not yet been made between the two optical counters or with the MOUDI, nor has any evaluation been done for the Angiola data.

In evaluating data from the different sizing instruments, care must be taken in how the particle diameter is defined. Particle size can be characterized in a number of ways, by mobility diameter, optical diameter or aerodynamic diameter. Mobility measurements are defined by the diameter that appears in Stokes' drag law, which gives the resistance force on a particle when its velocity differs from the airstream velocity. For a smooth, spherical particle, this resistance diameter is the same as the geometric particle diameter. SMPS measurements are based on mobility diameter, which depends on the electrical charge and the resistance diameter. The LasAir and Climet measurements are based on “optical diameter.” Optical diameter is an operational definition that refers to the amount of light scattered by the particle relative to a calibration aerosol. For CRPAQS the optical instruments were calibrated with dioctyl sebacate (refractive index = 1.45) and with polystyrene latex (refractive index = 1.59). Optical diameters depend on the characteristics of the instrument, such as the wavelength of the illuminating light and the geometry of the collection optics, as well as on the refractive index and size of the particle being measured. The MOUDI is an impactor, and measures aerodynamic diameter, which is dependent upon the bulk density of the particle as well as its geometric size.

When the measurements between the SMPS and the LasAir, or between the LasAir and the Climet, do not agree, then comparison with the nephelometry and MOUDI size distributions will be used to provide guidance as to the source of the discrepancy. These analyses will be most useful when temperature or relative humidity does not confound

the comparison. Based on these comparisons, we will select what data to use in the region of overlap in constructing a combined size distribution.

Sverdrup et al. (1982) identified three modes to the size distribution, roughly corresponding to the size ranges below 0.1 μm, 0.1-1 μm and above 1 μm. It should be noted that the instruments were selected for this study such that one instrument spans each of these three size ranges. Thus, evaluation of changes of the size distribution within a single mode will be reflected in the measurements by a single instrument, and thus will not be confounded by differences in sizing among the three instruments.

3.2. Subtask 2.8.2: Modal Parameter Characterization

The reduced size distribution data give the number concentration as a function of particle diameter. Examples of two such size distributions measured by the SMPS in Fresno in February, 2001 are shown in Figure 1. Here the data are plotted on a logarithmic particle diameter scale, and the area under the curve is directly proportional to the total number concentration. These two distributions have similar total number concentrations but differ significantly in other respects. The distribution on February 3 has a single mode centered near 0.1 μm whereas that on February 5 is comprised of two modes shifted toward smaller particle sizes.

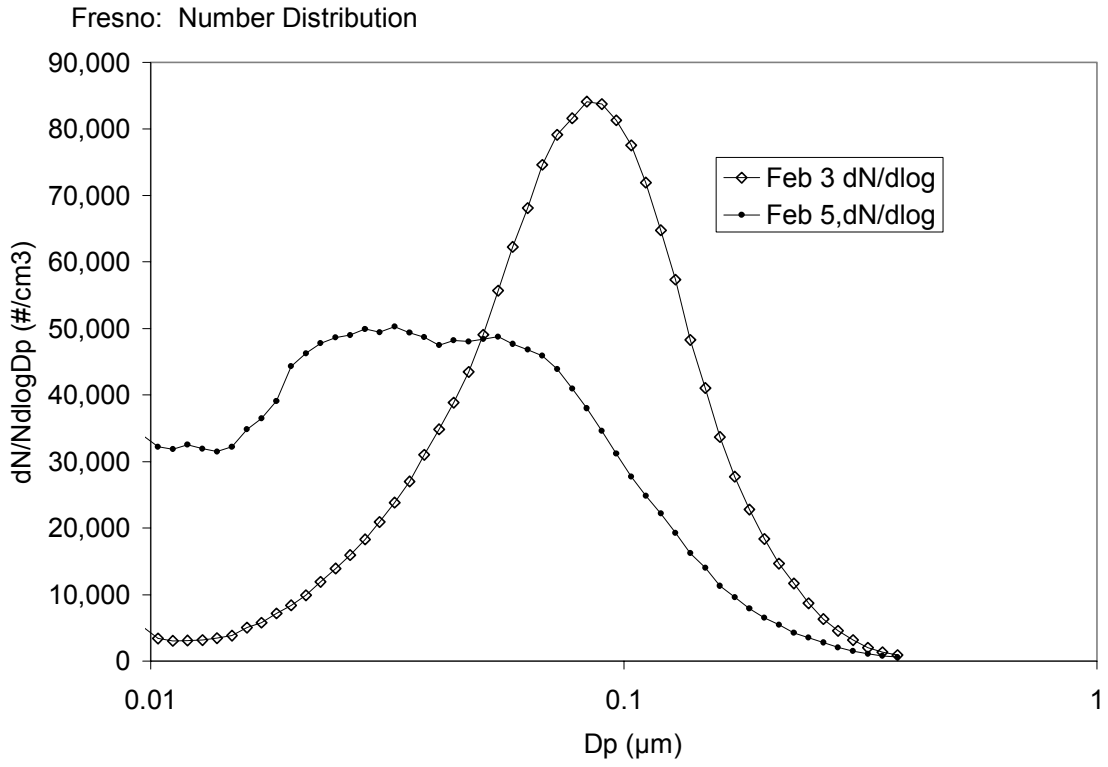

Figure 1: Two examples of number size distributions measured by the SMPS in Fresno in February, 2001. Though of similar total number concentration these two distributions differ significantly in mean size and distribution width as well as number of modes (see Table 2).

Size distributions may be expressed as particle surface area or volume, as shown in Figures 2 and 3, respectively. These data are derived from the number distribution under the assumption of spherical particles. The differences between the shapes of the two distributions are not as apparent in the volume distribution because the small particles present in the distribution of February 5 are not large contributors to the particle volume.

The question arises how one can characterize these distributions so that many distributions can be compared readily and meaningfully. What is of interest is not the number count in each of the 53 channels of data, but rather the overall characteristics such as the total number, the geometric mean diameter and the geometric standard deviation. Also of interest is the number of modes, or "bumps", in the distribution and the particle number, volume and diameter associated with each mode.

Size distributions are readily characterized by the following integral parameters, or moments:

$$M_n \equiv \int D_p^n \left(dN / d \log D_p \right) d \log D_p \qquad (1)$$

where M_n is defined as the nth moment, D_p is the particle diameter, and N is the number concentration.

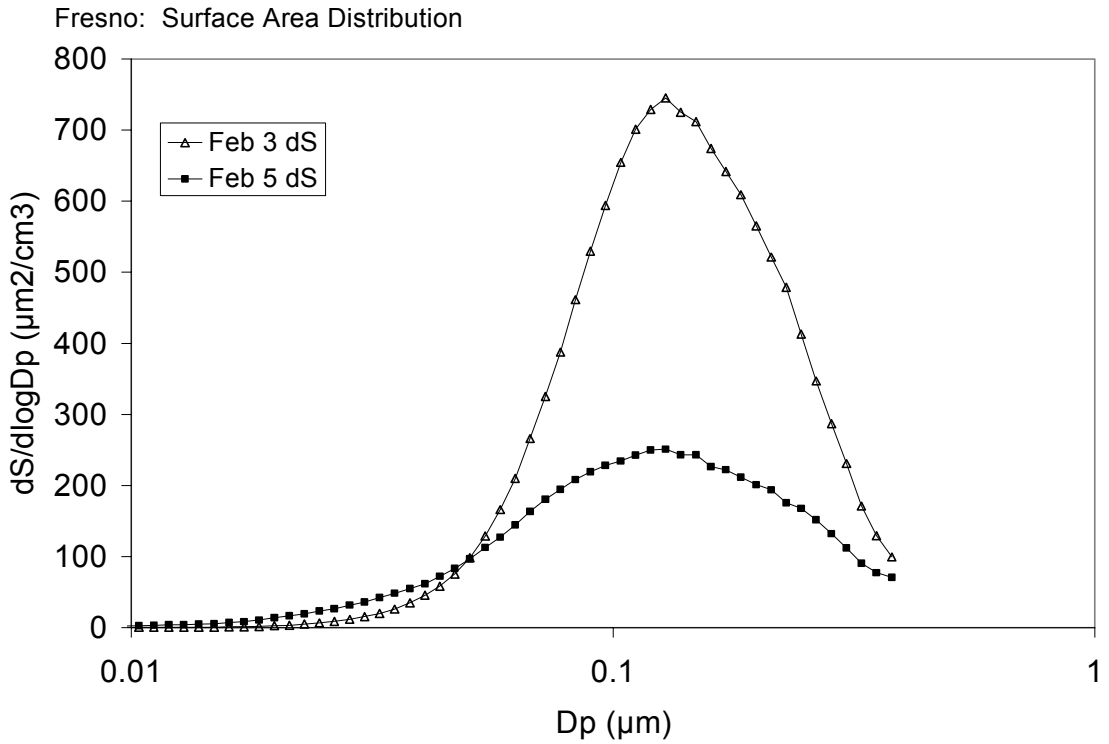

Figure 2: The two example distributions from Figure 1, shown in the surface area weighting. The shape difference is not as apparent but the size shift has translated to a large difference in total aerosol surface area (see Table 2).

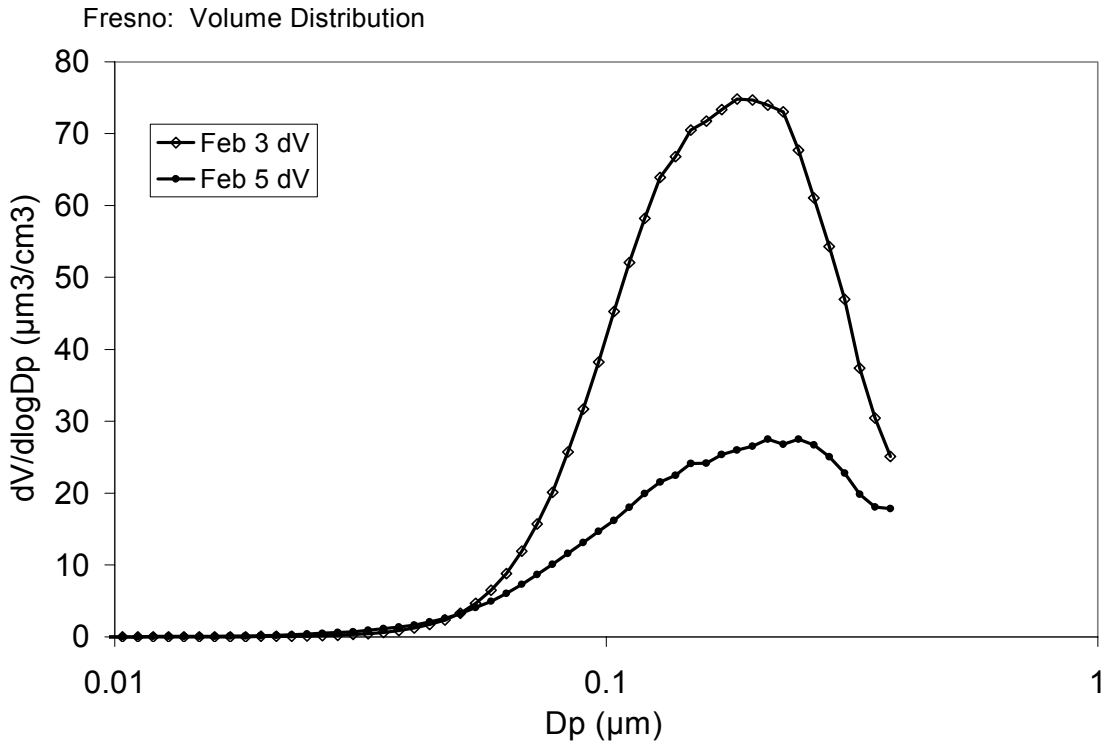

Figure 3: The two example distributions from Figure 1, shown in the volume weighting. The shape difference is not as apparent but the size shift has translated to a large difference in total aerosol volume (see Table 2).

The different moments weight the different modes of the distribution. Total number (n=0) is dominated by nuclei mode particles, below 0.1 μm in diameter. The surface area moment (n=2) is dominated by the accumulation mode, or particles between 0.1 and 1 μm. The volume moment (n=3) weights both the accumulation and coarse particle modes. One can construct a moment for n=4 which weights the coarse particle mode. These moments provide a straight forward means to compare size distributions without deconvoluting the distributions into separate modes.

The volume distributions of ambient particles are characterized by three major modes, the nuclei, accumulation and coarse particle modes. Each of these in turn can be comprised of one or more secondary modes. Each mode, or size range of the distribution, can be characterized by a mean or median size, and by the width of the distribution. The characteristic particle size may be expressed in any of the following ways:

Geometric number mean diameter
Geometric volume mean diameter
Number median diameter
Volume median diameter

Analogous definitions can also be constructed for other weightings of the distribution such as surface area. The geometric mean diameter $D_{g,n}$ for the nth weighting of the distribution is defined by

$$\log D_{g,n} \equiv M_n^{-1} \int \left(\log D_p\right) D_p^n \left(dN/d\log D_p\right) d\log D_p \quad . \tag{2}$$

The spread, or width, of the distribution is defined by its geometric standard deviation, $S_{g,n}$:

$$\log^2 S_{g,n} \equiv M_n^{-1} \int \left(\log D_p - \log D_{g,n}\right)^2 D_p^n \left(dN/d\log D_p\right) d\log D_p \quad . \tag{3}$$

When a size distribution is lognormal in shape, the geometric mean diameter and median diameters for a given distribution are equal, and the geometric standard deviation is the same for all weightings n of the distribution. When the distribution is not lognormal the geometric standard deviation can still be defined and measured through equation (3), but its value varies with the weighting of the distribution.

Table 2 shows these parameters are calculated for the size distributions of Figures 1-3. Note that the two distributions have similar total number concentrations but that of February 5 has a notably lower number median diameter and larger geometric standard deviation as seen in Figure 1. It also has notably less surface area and volume as shown in Figures 2 and 3.

Table 2. Size Distribution Parameters for SMPS Measurements of Figures 1 - 3.

Parameter	3-Feb	5-Feb
Total Number (#/cm^3)	49310.13	49134.76
Total Surface Area (μm^2/cm^3)	403.79	179.81
Total Volume (μm^3/cm^3)	40.50	16.67
Area/particle (μm^2)	8.19E-03	3.66E-03
Volume/particle (μm^3)	8.21E-04	3.39E-04
Number median diameter (μm)	0.07	0.04
Surface medain diameter (μm)	0.13	0.11
Volume median diameter (μm)	0.16	0.16
Geometric standard deviation, number distribution	1.18	1.30

The approach to be taken in deconvolution of the particle size distribution into separate modes is not straight forward when the number of modes per distribution is variable. Simply fitting the data to a sum of three lognormal distributions will not necessarily yield modes readily identified as nuclei, accumulation and coarse. It may be that the modes are best defined by their typical size range, and that the data be analyzed according to the

characteristic diameters within those ranges. The best approach for this data set will be determined as a part of this research effort.

3.3. Subtask 2.8.3: Spatial and Temporal Variability

The temporal variability of the size distributions will be evaluated through the integral and modal parameters defined in Subtask 2.8.2 above. The variability in number concentration, particle surface area and volume and modal diameters and widths can be displayed through time series plots. Of interest is the variability in intensive parameters, that is parameters such as the number median diameter or distribution width (as characterized by geometric standard deviation), as these are not directly dependent upon the overall particle concentration. Also of interest is the variation in ratios of extensive parameters, such as the ratio of the volume to number concentrations, or the ratio of accumulation mode surface area to nuclei mode number concentration. This latter parameter is important for assessing the magnitude of scavenging by the accumulation mode of newly injected or formed particles.

An example time series plot of size distribution data is given in Figure 4 for February 2001 at Fresno. The particle volume and number concentration both vary by a factor of 10 each day. By contrast, the ratio of these two extensive parameters, namely the average volume per particle, is less variable. Such information will be of importance in determining changes in the character of the aerosol rather than simply tracking changes in overall concentration.

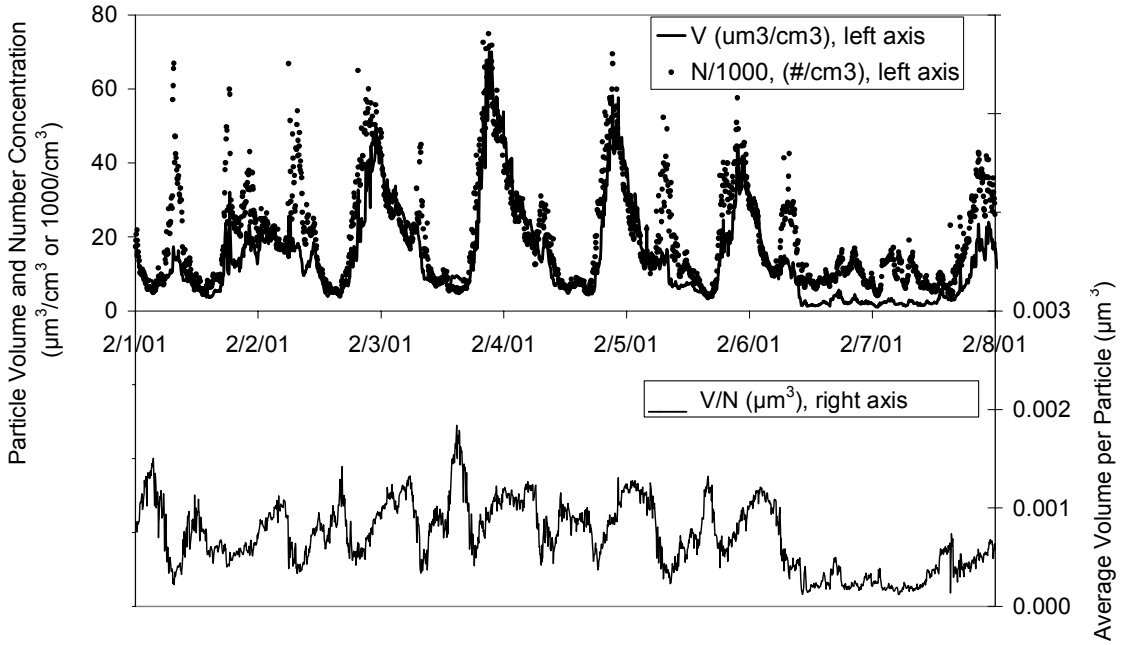

Figure 4: Time series plots of particle size distribution volume and number concentrations and their ratio for February, 2001 SMPS data. Note the greater variability of the extensive parameters (volume and number) comparted to the intensive parameter (average volume per particle).

The time scale on which each of these parameters change can be expressed by the standard deviation in the parameter as a function of the time interval over which the standard deviation is calculated. The variability is small when the interval of comparison is close to that of the measurement averaging time. The variability increases as the time interval increases. From this analysis one can infer a time constant that describes the rate at which the standard deviation increases with the comparison interval. Of interest is the relative comparison of the variability time scales among parameters and between sites.

3.4. Subtask 2.8.4: Synthesis and Manuscript Preparation

The results of the three tasks will be compared with other, readily-available time-resolved particle data at the sites. Comparison of the size distribution data with particle light scattering will be done as part of the Level 2 validation checks described in the first subtask (2.8.1). Of further interest is how the particle size distribution characteristics are related to the particle chemistry. Specific hypotheses to be tested are:

1) Are increases in black carbon concentrations related to increases in particle number concentrations?

2) Is the presence or absence of droplet mode accumulation aerosols related to the ratio of nitrate to black carbon concentration?

Black carbon is a primary constituent. Likewise, the nuclei mode particles, which dominate the total number concentrations, are attributed to fresh combustion sources. We will examine whether these two particle attributes are coincident in time.

Nitrate is hygroscopic, while freshly emitted black carbon is not believed to be hygroscopic. We will test whether the portion of the accumulation mode that can be assigned to the droplet mode is at all proportional to the relative ratio of these two constituents. Using the nephelometer data to infer the total PM2.5 mass, we will also examine the relationship of the droplet mode to the fraction of the PM2.5 mass that is attributable to nitrate.

These results will be summarized in an article to be submitted for peer review. We are willing to coordinate our submission to a journal selected by ARB for a specialty issue, if that is desired.

3.5. Subtask 2.8.5: Vertical Distributions at Angiola

At Angiola, the particle sizing data set includes coarse particle size distributions at three elevations, ground level, 50 m and 100 m. Measurements were made with three Climet optical particle counters, each of which provides sizing between 0.5 μm and 10 μm. The ground level instrument was used as part of the SMPS-LasAir-Climet particle sizing system. The other two instruments were located on the Angiola Tower. All three were equipped with a PM-10 inlet, which is designed to admit all particles below 10 μm for wind speeds of up to 10 m/s. The data from these instruments will play a key role in the understanding of the vertical mixing of coarse particles, as identified in Task 5.3.

The Climet optical counters measure particles from 0.5 to 20 μm in diameter. This covers the upper end of the accumulation mode, and all of the coarse mode that penetrates the PM-10 inlet. The inlet was deemed necessary because the high wind speeds expected on the tower would lead to variation in the aspiration efficiency of large particles by the instrument. Each of the Climets at Angiola was collocated with a nephelometer, and comparison will be made to this data. This will not be the same as the Level 2 validation described in the first subtask because the lower end of the accumulation mode size distribution is not measured, and this is important to light scattering. However, the measured light scattering should at least be as large as that derived from the Climet size distributions. These comparisons will ensure that the data will be useful to those who pursue Task 5.3.

In support of Task 5.3, we will provide the parameters that characterize the coarse particle size distribution. These include the integral moments, namely number concentration and volume concentration and the intrinsic variables including median diameters, and the value of the geometric standard deviation that characterizes the spread of the distribution. We will compare the simultaneous measurements at the three elevations at Angiola, to check for consistency among measurements, and consistency in the comparison to the nephelometery data. Analysis of the vertical profiles of the size distributions in terms of the meteorological regimes will be deferred to those pursuing Task 5.3. We will communicate with that team, and provide supporting paragraphs for an appropriate journal article, as requested.

3.6. Subtask 2.8.6: Reporting Requirements

A draft work plan based on this proposal and comments received will be submitted to ARB within one month of the receipt of an executed the contract. A revised workplan will be prepared based on input from the first data analysis workshop. Updates on progress will be summarized in monthly reports to ARB once work commences. A journal article will be prepared on the results of the first three tasks, and submitted in fall, 2003, under Task 2.3.4 above. A final report documenting the efforts on all tasks will be submitted in Acrobat and Word format as requested, together with ten hard copies, by December 2003.